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# CONTENTS

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*James D. Navratil and Franklin L. Oetting*

**Abstract.** The exothermic enthalpy of TRIS [tris (hydroxymethyl) aminomethane] with 0.1*M* hydrochloric acid at 298.15 K, has been determined under a variety of conditions using a modified LKB reaction calorimeter. The calorimeter and mode of operation were altered in various ways to ensure reliability. For example, a separate electrical energy measurement system was installed for comparison with the LKB system. The Regnault-Pfaundler and modified Dickinson calculation methods for the corrected temperature rise were also compared. Calorimetric results using a vented reaction vessel were compared to those using an unmodified vessel.

Our best enthalpy value of −7108 ±5 cal·mol$^{-1}$ for the standard TRIS reaction is compared with other TRIS results reported to date. An enthalpy of −7077 ±6 cal·mol$^{-1}$ was measured using hydrochloric acid solution saturated with carbon dioxide.

## INTRODUCTION

An LKB reaction calorimeter was obtained to measure various heats of reaction of interest to the nuclear industry. To ensure reliability of the calorimetric measurements and to guard against any possible systematic error in the calorimetric system, the exothermic heat of the standard reaction of TRIS [tris (hydroxymethyl) aminomethane with 0.1*M* hydrochloric acid was measured at 298.15 K.

Even though the reaction of TRIS with hydrochloric acid is considered to be a standard for solution calorimetry, there is a slight discrepancy in the heat value. The certified value for the TRIS-hydrochloric acid reaction as given by the National Bureau of Standards[1] is almost 0.1% more exothermic than previously reported high precision results.[2,3] Hopefully the results obtained with our calorimeter would help to resolve the small discrepancy.

Prosen and Kilday[1] have found that anomalous results on the TRIS-hydrochloric acid reaction are obtained if the reaction vessel is not vented. Hubbard, et al.[4] reported a less exothermic reaction if carbon dioxide is present in a vented system. Therefore, our intention was to examine the TRIS-hydrochloric acid reaction in our calorimeter with regard to these side effects to better understand the capabilities of the instrument and also to become fully aware of its limitations.

To guard against any systematic error in the calorimetric system, an auxiliary electrical energy measurement system was installed for comparison with the unit commercially available on the LKB reaction calorimeter. Also, an examination of two different modes of temperature rise calculations, the modified Dickinson method[5] and the Regnault-Pfaundler method,[6] was made to determine which method best suited our needs.

## SUMMARY AND CONCLUSIONS

The exothermic enthalpy of TRIS [tris (hydroxymethyl) aminomethane] with 0.1*M* hydrochloric acid at 298.15 K, has been determined under a variety of conditions using a modified LKB reaction calorimeter. The calorimeter and mode of operation were altered in various ways to ensure reliability. For example, a separate electrical energy measurement system was installed for comparison with the LKB system. No significant difference in results was observed between the two energy measurement stations. The Regnault-Pfaundler and modified Dickinson calculation methods for the corrected temperature rise were also compared. The latter method was found less precise than the former method and the two gave comparable results for fast reactions only. Calorimetric results using a vented reaction vessel were compared to those using an unmodified vessel. The results were similar and showed that the unmodified vessel was indeed vented.

Our best enthalpy value of −7108 ±5 cal·mol$^{-1}$ for the standard TRIS reaction is in excellent agreement with other TRIS results reported to date. An enthalpy of −7077 ±6 cal·mol$^{-1}$ was also measured using hydrochloric acid solution saturated with carbon dioxide.

## EXPERIMENTAL

### Materials

The "Solution Calorimetry Standard," TRIS, NBS Standard Reference Material No. 724, stated purity of 99.94 ±0.01 mole percent, was stored over saturated magnesium nitrate solution at least 2 weeks prior to use.[7] The molar mass of 121.137 g·mol$^{-1}$, density of 1.35 g·cm$^{-3}$ for weight correction to *in vacuo*, and purity of 100%, were used.

Solutions of 0.1*M** hydrochloric acid were prepared from Baker "Ultrex" hydrochloric acid and doubly distilled water. During storage, the hydrochloric acid was protected against carbon dioxide absorption by use of sodium hydroxide-coated asbestos in guard-tubes.

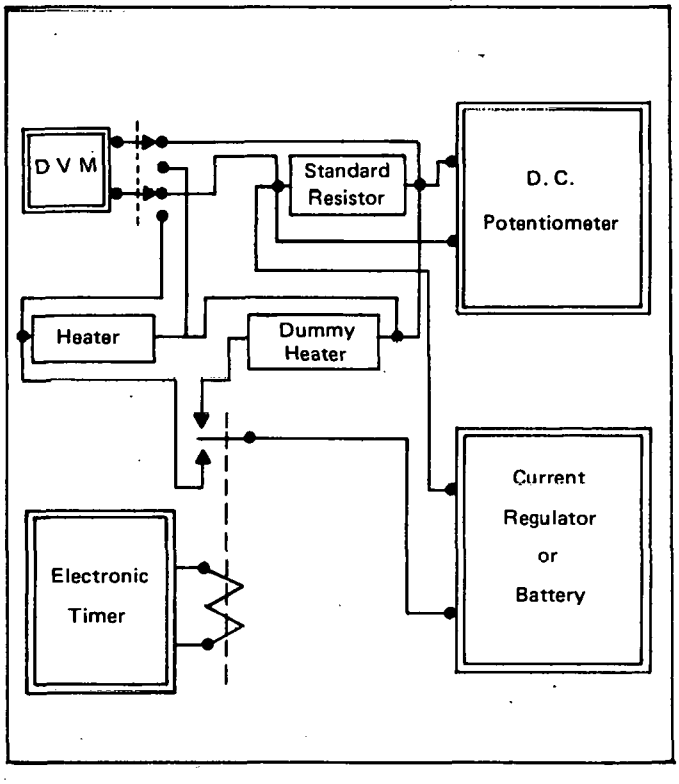
## Calorimeter and Procedure

An LKB 8700-1 reaction calorimeter of the isoperibol type was used for the measurements. Various components such as the standard resistors, wheatstone bridge, potentiometer, timer, and standard cell were checked or calibrated by certified components of the Physical Metrology Laboratory at Rocky Flats, which are traceable to standards at the National Bureau of Standards. The stability of the constant-temperature bath was found to be ±0.001°C during an 8-hour period. LKB claims a precision of ±0.003% and an accuracy <0.02%, in general, for the heat measurements.

The calorimeter heater circuit was modified as shown in Figure 1 to include an auxiliary electrical energy measurement station and the capability of increased power from batteries. The extra measurement unit was installed for comparison with the LKB system and was necessary for power measurements when the LKB power supply was disconnected and replaced by two 12-volt batteries in serie The increased power was necessary to better match the calibration resistance-time curves with the reaction curves. However, for proper operation of the heater, the power was kept below one watt.

*M = 1 mol·dm$^{-3}$; cal = 4.184 abs joules.

**Figure 1. Simplified Wiring Schematic of Heater.**




During most of the calibration runs, the LKB electrical energy measurement unit was used simultaneously with the auxiliary measurement unit. The auxiliary station consisted of a Hewlett-Packard 3450A Multi-Function Meter, coupled with a 5050B Digital Recorder, which recorded voltages across the heater and standard resistor via a relay switching every 4 to 6 seconds.

Temperature measurements were made with a thermistor which was calibrated in degrees at six different temperatures between 24.9 and 25.5°C with a National Bureau of Standards calibrated platinum-resistance thermometer. These measurements were fitted to both a straight line by least squares and to the equation

$$R = A \cdot e^{B/T} \qquad (1)$$

where R and T are the resistance and temperature, respectively, and A and B are constants obtained by a computer fit of the data. No significant difference in calibrations, using either equation, was observed.

A typical experiment consisted of breaking a one milliliter glass ampoule, containing 0.5 g of TRIS, into 100 ml of 0.1*M* hydrochloric acid after allowing the calorimetric system to come to thermal equilibrium (20 to 30 minutes). To properly define the resistance-time curve, about ten resistance and time measurements were taken during the initial and final periods, and as close together as possible during the main period. After each run, the side of the reaction vessel was cooled to the pre-reaction temperature with cool, dry air. At least two calibration runs were performed either before or after the reaction experiment where the mean or initiation temperature was 298.15 ±0.001 K, respectively.

## Calculation Methods

A combined computer program was used to calculate heats of reaction by treating the experimental data in two ways. The program contained both the method of Dickinson[8] as modified by Fitzgibbon et al.[5] and the Regnault-Pfaundler method, as described by Wadsö,[6] for the calculation of the corrected temperature rise.

A typical resistance-time curve for an experiment, shown in Figure 2, visualizes the terms of the equation,

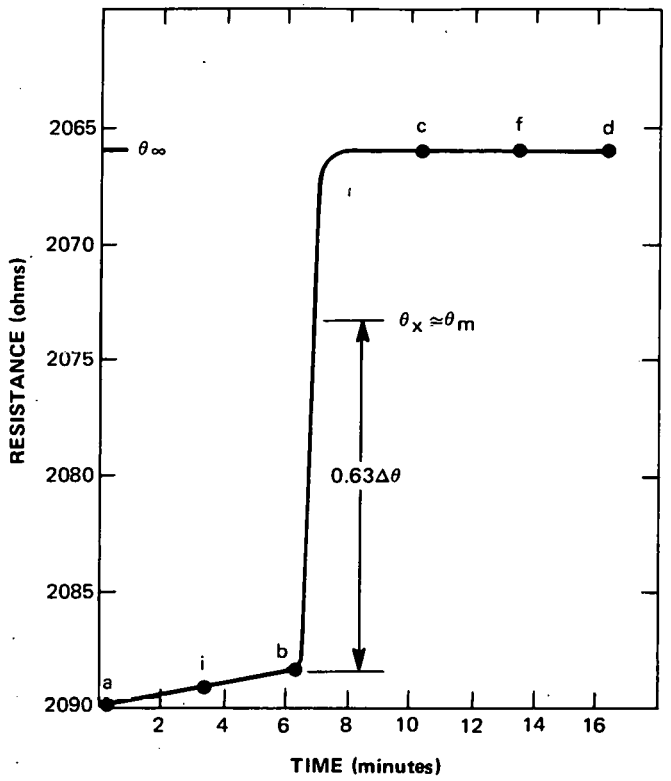



**Figure 2. Resistance-Time Curve for the TRIS-Hydrochloric Acid Reaction.**

**Table 1. Definition of Symbols.**

| | |
|---|---|
| $\theta$: | Resistance in ohms at beginning of initial period ($\theta_a$), mean of initial period ($\theta_i$), start of main period ($\theta_b$), mean of the main period ($\theta_m$), end of main period ($\theta_c$), mean of final period ($\theta_f$), end of final period ($\theta_d$), and at equilibrium ($\theta_\infty$). |
| t: | Time in minutes with subfixes corresponding to the same periods as the $\theta$ values. |
| g: | Slope $d\theta/dt$, of the initial ($g_1$), main ($g_2$), and final ($g_3$) periods. |
| A: | Intercept at t = 0 of the initial ($A_1$), main ($A_2$), and final ($A_3$) periods. |
| K: | Heat leakage constant = $(g_1 - g_3)/(\theta_f - \theta_i)$. |
| $\Delta t$: | Calibration time in seconds. |
| $EMF_{(h)}$: | EMF across heater. |
| $EMF_{(s)}$: | EMF across standard resistor. |
| i: | Current. |
| $R_{(s)}$: | Resistance of standard resistor. |
| $R_{(HL)}$: | Resistance of the heater leads. |
| n: | Number of moles. |

$$\Delta R = \theta_c - \theta_b - [g_1 (t_x - t_b) - g_3 (t_c - t_x)] \quad (2)$$

where $\Delta R$ is the corrected resistance change of the modified Dickinson method. The $t_x$ value was calculated from the equation,

$$t_x = (\theta_x - A_2)/g_2 \quad (3)$$

where $\theta_x$ was taken as $\theta_x = \theta_b - (\theta_b - \theta_c)\,0.5$ and $\theta_x = \theta_b - (\theta_b - \theta_c)\,0.63$ for calibration and reaction runs, respectively. The remaining terms are defined in Table 1. The terms within the brackets of Equation 2 are the corrections for the heat of stirring, heat leakage, and heat generated by the thermistor. All the $\theta$ and t values in the initial and final periods were fitted to a straight line by a linear-least-squares sub-routine to obtain the corresponding intercept at t = 0 and mean slope values. The initiation time ($t_b$) of the reaction or calibration was used to calculate the corresponding $\theta_b$ value by use of the equation,

$$\theta_b = A_1 + g_1 t_b \quad (4)$$

Since the resistance change in the final period was small, $\theta_c$ was taken as the first resistance value where a steady state condition was reached. Selection of the $\theta_c$ value was confirmed by comparing the uniformity of $\Delta \ln (\theta - \theta_\infty)/\Delta t$ values calculated for the last five data points in the main period, and all the data points in the final period after the method of Coughlin.[9] Next, $t_c$ was calculated from the relation,

$$t_c = (\theta_c - A_3)/g_3 \quad (5)$$

Only a few points in the linear portion of the main period (40 to 70% of $\Delta R$) were used to calculate $A_2$ and $g_2$.

The Regnault-Pfaundler method for the calculation of the corrected temperature rise was taken from Wadsö.[6] Equations 6 and 7 are equivalent and give the corrections for the heat of stirring, heat leakage, and heat generated by the thermistor.

$$\Delta\theta_1 = [g_1 - K(\theta_m - \theta_i)]\ (t_c - t_b) \quad (6)$$

$$\Delta\theta_2 = [g_3 - K(\theta_m - \theta_f)]\ (t_c - t_b) \quad (7)$$

The symbolism in Equations 6 and 7 are defined in Table 1. The mean resistance, $\theta_m$, is determined by the trapezoid rule given by the equation,

$$\theta_m = \frac{(t_2 - t_1)\left[\frac{(\theta_1 - \theta_2)}{2}\right] + (t_3 - t_2)\left[\frac{(\theta_2 - \theta_3)}{2}\right] + \cdots +}{(t_2 - t_1) + (t_3 - t_2) + \cdots +} \quad \frac{(t_{n+1} - t_n)\left[\frac{(\theta_n - \theta_{n+1})}{2}\right] + \cdots}{(t_{n+1} - t_n) + \cdots} \tag{8}$$

Finally, the corrected resistance change is given by either of the following equivalent equations,

$$\Delta R_1 = \theta_c - \theta_b - \Delta\theta_1 \tag{9}$$

$$\Delta R_2 = \theta_c - \theta_b - \Delta\theta_2 \tag{10}$$

The energy equivalent, $\epsilon$, given by the equation,

$$\epsilon = Q/\Delta T \tag{11}$$

was utilized since it was not always possible to match the calibration and experimental resistance-time curves exactly. The value $\Delta T$, the corrected temperature rise, is defined by the equation,

$$\Delta T = \frac{\Delta R\, T_m^2}{C\, \theta_m} \tag{12}$$

and is used to account for the nonlinear relationship between changes of resistance and degrees; $T_m$ and $\theta_m$ are the mean temperature and resistance values of the main period, respectively, where the former is calculated from Equation 1, and C = 3348, a constant calculated from the calibration of the thermistor in degrees. The calibration energy, Q, is given by the equations,

$$Q = \frac{\Delta t\left[\left(\frac{R_{(s)} \cdot EMF_{(h)}}{EMF_{(s)}}\right) - R_{(HL)}\right] i^2}{4.184\ J \cdot cal^{-1}} \tag{13}$$

$$Q = \frac{\Delta t \cdot EMF_{(h)} \cdot EMF_{(s)}}{R_{(s)} \cdot 4.184\ J \cdot cal^{-1}} - \frac{R_{(HL)}\left(\frac{EMF_{(s)}}{R_{(s)}}\right)^2 \Delta t}{4.184\ J \cdot cal^{-1}} \tag{14}$$

Equation 13 corresponds to data taken from the LKB measurement station. A current of 0.02 amp is first set by adjusting the current from the power supply until the EMF drop across the standard resistor (49.996 ohms) is 1.00000 V. Then the EMF across the heater is measured. Five different standard resistors can be connected in the circuit for the calibration runs and in each case the current is adjusted prior to the run until the potential drop across the standard resistance is 1.0000 V. Calibration time ($\Delta t$) is measured by an electronic timer. The heater lead resistance [$R_{(HL)}$], 0.0130 ohms, was taken from half the product of the lead length (10 cm) and lead resistance (0.26 ohm/meter). Equation 14 is used for the DVM measurements where the EMF drop across the heater and standard resistor is measured. The remaining terms are defined in Table 1. The final $\Delta H$ ($cal \cdot mol^{-1}$) value was calculated from the equation,

$$\Delta H = \frac{\epsilon(\Delta T)_{exp}}{n} \tag{15}$$

where $\Delta T_{exp}$ is the corrected temperature rise of the experiment.

## RESULTS AND DISCUSSION

Table 2 contains the mean and twice the standard deviation of the mean, $2\,[\Sigma\, d^2/n(n-1)]^{1/2}$, for each group of experiments performed under a variety of conditions (details of the individual experiments are contained in Appendix I). The operational or experimental conditions were changed after some groups of measurements. Calibration of the standard cell and DVM was performed prior to experiments 25 and 12, respectively. A new reaction

**Table 2. Average Enthalpy Results Obtained Under Various Conditions.**

| Conditions | $-\Delta H_{298.15K}$ ($cal \cdot mol^{-1}$) |
|---|---|
| [a]Regnault-Pfaundler calculation method | 7111.2 ±3.5 |
| [a]Modified Dickinson calculation method | 7111.4 ±3.8 |
| [b]Initial Experiments (2-12). | 7114.8 ±3.5 |
| Experiments 13-15 | 7112.4 ±0.2 |
| Vented Reaction Vessel Experiments (17-19) | 7117.6 ±3.7 |
| Battery Power Source (21-22) | 7115.9 ±2.5 |
| [c]Final Experiments (25, 26, 29, 32, 35, 36, 38) | |
| LKB Station | 7106.6 ±4.9 |
| DVM Station | 7108.7 ±4.9 |
| $CO_2$ Experiments (28, 31, 33, 34, 37) | 7077.4 ±6.0 |

[a]All experiments were averaged except for the values from the DVM power measurements and $CO_2$ experiments.
[b]Average results are taken from Regnault-Pfaundler calculations.
[c]Results shown are from LKB and DVM power measurements, respectively.

vessel was introduced before experiment 25. The hydrochloric acid concentrations were 0.0991 and 0.0998*M* for experiments numbers 2 through 12 and 13 through 38, respectively. The experiments, numbered 1, 5, 11, 16, 20, 23, 24, and 27, were omitted because of instrument or experimental difficulties and/or anomalous heat leakage constants.

The corrections applied to the results included a temperature correction to 25.00°C for experiments 2 through 22. Corrections for the heat of ampoule breaking were stated by the manufacturer as less than 0.002 calories for 90% of the ampoules, and our measurements on several empty ampoules confirmed their result. Since there was no change in air pressure upon breaking the ampoules during the TRIS experiments, only small condensation and vaporization corrections need be made. The condensation correction can be neglected since there is no change in ionic strength during the neutralization reaction of TRIS. The vaporization correction was calculated as 0.0060 and 0.0142 calories for conditions relating to the TRIS experiments and empty ampoule breaking experiments, respectively. The heat of breaking the ampoules and saturation of the air in the ampoules with water vapor was determined simultaneously by breaking 14 ampoules containing air (22% relative humidity). The measured endothermic heat was 0.0113 ±0.0068 calories. The combined heat of vaporization and breaking correction for the TRIS experiments (0.0042 calories) was calculated by multiplying the measured value (0.0113 calories) by the ratio of the calculated vaporization heats (0.0060/0.0142), under the respective conditions. The correction in calories (1.0), obtained by dividing the combined value (0.0042) by the mean number of moles (0.00411), was added to the enthalpy values in Table 2.

As shown in Table 2, the results calculated from the Regnault-Pfaundler and modified Dickinson methods are in excellent agreement. Hill et al.[2] also reported that within experimental uncertainties, the two methods gave identical results. However, it is of interest to note that the results from using the modified Dickinson method are less precise as shown by the error limits. This is probably not too surprising since the modified Dickinson method does involve the approximation of $\theta_x$. Also, the approximate method should be avoided for reaction times greater than 5 minutes;[6] for example, heats of solution of beryllium in 1*M* $H_2SO_4$, with reaction times of ~20 minutes, were 1.3 percent less exothermic using the modified Dickinson method as compared to the Regnault-Pfaundler method.[10] However, the Regnault-Pfaundler method is sensitive to erroneous heat leakage constants.[6]

The results of the initial experiments, 2-12 (−7114.8 ±3.5) compared to the final experiments, 25, 26, 29, 32, 35, 36, and 38, (−7106.6 ±4.9) are significantly different. The former experiments were obtained under conditions where the TRIS weights were only to four places, large temperature corrections to 25.00°C were necessary, and where condensation of liquid on the neck of the reaction vessel was possible since the bath temperature was not maintained above the final reaction temperature. The latter group of experiments was done under conditions which avoided all these experimental difficulties. In addition, the cooling tube was altered to direct the stream of cool air at the base of the reaction vessel to prevent condensation of liquid on the neck of the vessel, and the outer can surrounding the vessel was evacuated to 30-100 microns during the final group of experiments to eliminate significant heat transfer by convection and conduction. It was thought that the last experimental condition was the most important cause for the difference in the initial and final experiments since the magnitude of free convection for our calorimeter was a significant factor. For the LKB calorimeter, $\ell^3 (T_1 - T_2)$ was calculated as 65 $cm^3$ deg., where $\ell$ is the width of the gas space, and $T_1 - T_2$ is the observed temperature change. For air near room temperature and atmospheric pressure, $\ell^3 (T_1 - T_2) < 11$ $cm^3$ deg K assures that heat transfer is directly proportional to temperature difference.[11] Therefore, based on the above, it was felt that the final group of experiments were the most reliable.

Comparison of the next two sets of experiments (13-15) versus (17-19) in Table 2 shows the effect of venting the reaction vessel (through notches in the gasket located between the vessel and the top of the outer can) over the normal venting through the stirrer. The difference in the results is probably not significant, indicating that our calorimeter is indeed vented and not sensitive to the pressure effects reported by others.[1]

Calibration runs in the next group of experiments (21-22) were obtained using a battery power source where calibration times were comparable to reaction times. The difference of these results compared to the above results is probably not significant since only two experiments were performed. Also, since an energy equivalent was utilized in the calculations, there should not be any difference in results when the calibration curve differs somewhat from the experimental curve.[6]

The $CO_2$ experiments were obtained using hydrochloric acid purged with carbon dioxide. The 0.0998*M* HCl increased in proton concentration to 0.118*M*. Our enthalpy values (−7077.4 ±6.0 cal·$mol^{-1}$) are in agreement with the results of the Argonne workers[4] (−7082 cal·$mol^{-1}$). Figure 3 shows resistance-time plots of the last part of the main period and the final period of representative normal

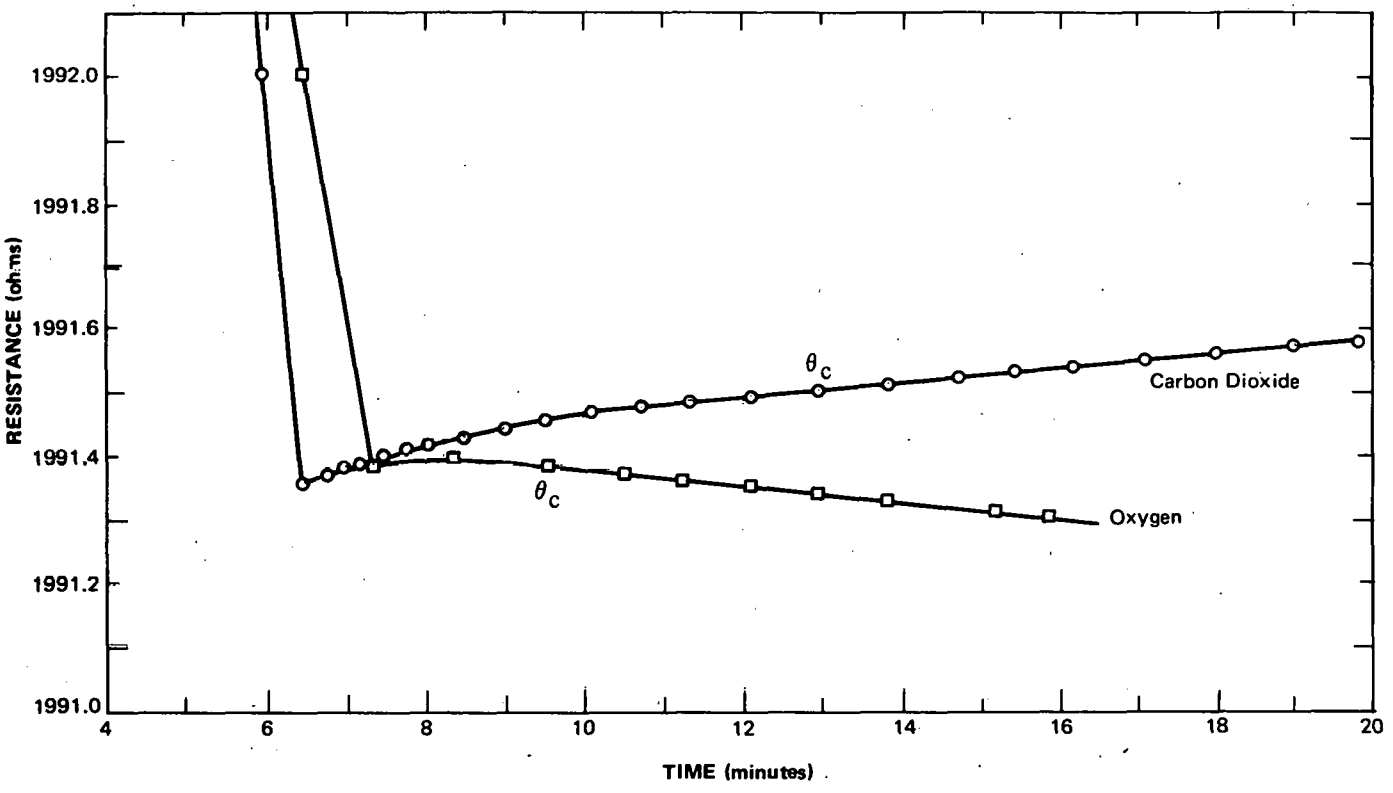



**Figure 3. Resistance-Time Curves of Reaction Runs using Oxygen and Carbon Dioxide Purged HCl.** ($\theta_c$ is resistance value where steady state conditions were reached.

and $CO_2$ experiments. In the $CO_2$ experiments, equilibrium was not attained right after the main period as in the normal experiments, and the slope is reversed. Based on this and the increased proton concentration in the $CO_2$ purged HCl, there is probably a slow-endothermic reaction taking place between the TRIS and $H_2CO_3$, thus giving low enthalpy results. Therefore, since the reaction of TRIS with carbon dioxide containing hydrochloric acid gives low results, investigators should be aware of this effect. However, when the system is not vented, the presence of $CO_2$ reportedly gives more exothermic results.[1]

The two electrical energy measurement stations are compared in the final group of experiments shown in Table 2. There was no significant difference in results between the two energy measurement stations which indicates the LKB station was operating properly. The auxiliary unit did indicate an erroneous calibrated standard cell in one group of experiments, and an erratic current owing to power source fluctuations in another case. Therefore, it did prove as a valuable check on the LKB electrical energy measurements.

Since the final group of experiments (25, 26, 29, 32, 35, 36, and 38) were thought the most reliable, the mean result ($-7108 \pm 5$ cal·mol$^{-1}$) will be taken as our best value.

Table 3 compares our corrected best enthalpy value with reported high precision results. The first result[12] was corrected for a reported calculation error.[13] The results of the Lund workers[2,12,15,17] using a constant-temperature-environment-type calorimeter, and Gunn[3,14] using a rocking bomb calorimeter, are in excellent agreement and were reproduced over a period of 5 years. Furthermore, most of the results shown in Table 3 are in excellent agreement. This is very impressive since the TRIS used was of different

**Table 3. Comparison of our Average Enthalpy Value with Reported Results.**

| Investigator | $-\Delta H_{298}$ cal·mol$^{-1}$ |
|---|---|
| Irving and Wadsö[12] (1964) | 7108 ±4 |
| Gunn[14] (1965) | 7107 ±1 |
| Sunner and Wadsö[13] (1966) | 7111 ±2 |
| Vacca and Arenare[15] (1967) | 7109 ±1 |
| Fitzgibbon and Holley[16] (1968) | 7111 ±5 |
| Hill, Öjelund, and Wadsö[2] (1969) | 7109 ±1 |
| Gunn[3] (1970) | 7107 ±1 |
| Laynez, Ringner, and Sunner[17] (1970) | 7110 ±1 |
| Hubbard, et al.[4] (1971) | 7109 ±2 |
| Kilday and Prosen[1] (1971) | 7116 ±1 |
| Brunetti, Prosen, and Goldberg[18] (1971) | 7119 ±3 |
| Robie and Hemingway[19] (1972) | 7098 ±11 |
| Our Work (1972) | 7108 ±5 |

purity, different calculation methods were used, calibrations in relation to experiments were performed differently, etc. Therefore, it appears that the TRIS-HCl reaction is the most convenient one available to check the performance of reaction calorimeters compared to previous standards.[14]

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**APPENDIX I. Enthalpy of Neutralization of TRIS in 100.0 ml of 0.1*M* HCl.**

| Experiment Number and Stirring[a] | Mass of TRIS (g) | K[b] ($10^{-5}$) | R.P.[c] (cal·Ω$^{-1}$)[c] Before | R.P.[c] (cal·Ω$^{-1}$)[c] After | M.D.[c] (cal·Ω$^{-1}$)[c] Before | M.D.[c] (cal·Ω$^{-1}$)[c] After | Δθ(Ω)[d] | θ[e] (Ω) | ΔT[f] ($10^{-2}$ °C) | Corr. to[g] 298.15K (cal·mol$^{-1}$) | $-\Delta H_{298.15\,K}$ (cal·mol$^{-1}$) R.P.[h] | $-\Delta H_{298.15\,K}$ (cal·mol$^{-1}$) M.D.[h] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2L | 0.5124 | 606 | 98.863 | – | 98.899 | – | 0.964 | 22.132 | 30.298 | +28.9 | 7110.6 | 7094.7 |
| | | 609 | – | – | – | – | 0.904 | | 30.216 | | – | – |
| 3L | 0.5753 | 621 | – | 99.131 | – | 99.188 | 0.232 | 25.860 | 34.020 | +10.4 | 7112.0 | 7111.3 |
| | | 624 | – | – | – | – | 0.215 | | 33.997 | | – | – |
| 4M | 0.5492 | 603 | 99.028 | 99.169 | 99.083 | 99.206 | 0.119 | 24.779 | 32.422 | +16.1 | 7102.7 | 7109.0 |
| | | 620 | – | – | – | – | 0.130 | | 32.436 | | – | – |
| 6H | 0.4868 | 613 | – | 99.157 | – | 99.190 | 0.003 | 22.266 | 28.823 | + 4.7 | 7116.1 | 7117.2 |
| | | 664 | – | – | – | – | 0.007 | | 28.818 | | – | – |
| 7H | 0.4954 | 618 | – | 99.168 | – | 99.198 | 0.012 | 22.677 | 29.338 | + 4.4 | 7119.2 | 7113.8 |
| | | 671 | – | – | – | – | 0.035 | | 29.307 | | – | – |
| 8H | 0.4760 | 644 | – | 99.130 | – | 99.164 | 0.040 | 21.688 | 28.189 | + 6.8 | 7117.7 | 7118.0 |
| | | 673 | – | – | – | – | 0.033 | | 28.180 | | – | – |
| 9H | 0.4465 | 654 | – | 99.151 | – | 99.200 | 0.112 | 20.198 | 26.399 | + 9.0 | 7110.6 | 7109.5 |
| | | 670 | – | – | – | – | 0.099 | | 26.382 | | – | – |
| 10M | 0.4371 | 672 | 98.963 | 99.096 | 99.004 | 99.104 | 0.126 | 19.858 | 25.886 | +11.2 | 7116.0 | 7120.0 |
| | | 666 | – | – | – | – | 0.133 | | 25.894 | | – | – |
| 12M | 0.58456 | 604 | 99.642 | – | 99.705 | – | 0.032 | 26.478 | 34.382 | +19.5 | 7118.9 | 7121.1 |
| | | 602 | – | – | – | – | 0.024 | | 34.371 | | – | – |
| 13M | 0.50167 | 604 | – | – | – | – | 0.072 | 23.199 | 29.588 | – 0.47 | – | – |
| | | 606 | 99.446 | 99.639 | 99.454 | 99.642 | 0.071 | | 29.590 | | 7111.4 | 7112.2 |
| 14M | 0.55161 | 598 | – | – | – | – | 0.062 | 25.500 | 31.064 | – 0.90 | – | – |
| | | 602 | 99.461 | 99.667 | 99.487 | 99.669 | 0.069 | | 32.529 | | 7111.6 | 7110.7 |
| 15M | 0.56031 | 601 | – | – | – | – | 0.039 | 25.879 | 33.050 | – 0.74 | – | – |
| | | 610 | 99.385 | 99.681 | 99.470 | 99.701 | 0.043 | | 33.044 | | 7111.2 | 7113.7 |
| [i]17M | 0.50460 | 612 | – | – | – | – | 0.093 | 23.380 | 29.762 | – 1.44 | – | – |
| | | 619 | 99.505 | 99.657 | 99.513 | 99.667 | 0.091 | | 29.764 | | 7113.6 | 7114.7 |
| [i]18M | 0.49796 | 608 | – | – | – | – | 0.064 | 23.059 | 29.404 | + 5.26 | – | – |
| | | 609 | 99.464 | – | 99.471 | – | 0.069 | | 29.399 | | 7120.0 | 7119.2 |
| [i]19M | 0.49615 | 598 | – | – | – | – | 0.068 | 22.969 | 29.270 | + 4.78 | – | – |
| | | 605 | 99.511 | – | 99.467 | – | 0.067 | | 29.272 | | 7116.3 | 7113.5 |
| [j]21M | 0.50001 | 600 | – | – | – | – | 0.071 | 23.149 | 29.482 | – 1.87 | – | – |
| | | 618 | 99.579 | 99.731 | 99.576 | 99.722 | 0.077 | | 29.475 | | 7116.2 | 7113.9 |
| [j]22M | 0.50279 | 628 | – | – | – | – | 0.024 | 23.204 | 29.643 | – 0.88 | – | – |
| | | 595 | 99.542 | 99.687 | 99.504 | 99.698 | 0.041 | | 29.622 | | 7113.6 | 7107.4 |
| 25H | 0.50149 | 610 | – | 105.29 | – | 105.33 | 0.088 | 22.315 | 27.930 | 0.0 | 7107.8 | 7106.3 |
| | | 630 | – | 105.32 | – | 105.30 | 0.071 | | 27.968 | | 7109.7 | 7114.3 |
| 26H | 0.50008 | 611 | – | 105.19 | – | 105.23 | 0.076 | 22.237 | 27.862 | 0.0 | 7100.0 | 7102.5 |
| | | 616 | – | 105.21 | – | 105.24 | 0.075 | | 27.864 | | 7101.1 | 7103.6 |
| [k]28H | 0.49828 | 605 | – | 105.26 | – | 105.30 | 0.022 | 21.958 | 27.633 | 0.0 | 7071.3 | 7072.9 |
| | | 613 | – | 105.26 | – | 105.30 | 0.018 | | 27.628 | | 7071.2 | 7072.7 |
| 29H | 0.47340 | 642 | – | 105.21 | – | 105.24 | 0.099 | 21.086 | 26.378 | 0.0 | 7101.6 | 7107.0 |
| | | 630 | – | 105.25 | – | 105.28 | 0.089 | | 26.390 | | 7103.9 | 7109.4 |
| 30H | 0.50402 | 629 | – | – | – | | 0.116 | 22.436 | 28.064 | 0.0 | – | – |
| | | 640 | – | 105.25 | – | 105.25 | 0.110 | | 28.071 | | 7098.7 | 7101.0 |
| [k]31H | 0.49663 | 598 | – | – | – | – | 0.060 | 21.969 | 27.543 | 0.0 | – | – |
| | | 617 | – | 105.23 | – | 105.27 | 0.062 | | 27.541 | | 7069.7 | 7071.8 |
| 32H | 0.50359 | 662 | – | 105.26 | – | 105.27 | 0.098 | 22.426 | 28.074 | 0.0 | 7107.9 | 7112.4 |
| | | 678 | – | 105.28 | – | 105.30 | 0.088 | | 28.088 | | 7109.9 | 7114.2 |
| [k]33H | 0.50246 | 701 | – | 105.26 | – | 105.33 | 0.058 | 22.116 | 27.878 | 0.0 | 7074.6 | 7076.7 |
| | | 688 | – | 105.30 | – | 105.37 | 0.049 | | 27.867 | | 7077.1 | 7079.3 |
| [k]34H | 0.50164 | 711 | – | 105.23 | – | 105.23 | 0.038 | 22.107 | 27.841 | 0.0 | 7074.9 | 7072.3 |
| | | 696 | – | 105.26 | – | 105.26 | 0.030 | | 27.831 | | 7077.1 | 7074.5 |
| 35H | 0.50166 | 696 | – | 105.15 | – | 105.17 | 0.079 | 22.307 | 27.948 | 0.0 | 7096.4 | 7097.6 |
| | | 712 | – | 105.19 | – | 105.20 | 0.078 | | 27.949 | | 7098.6 | 7100.0 |

**APPENDIX I. (continued)**

| Experiment Number and Stirring[a] | Mass of TRIS (g) | K[b] ($10^{-5}$) | R.P.$\epsilon$ ($cal \cdot \Omega^{-1}$) Before | R.P.$\epsilon$ ($cal \cdot \Omega^{-1}$) After | M.D.$\epsilon$ ($cal \cdot \Omega^{-1}$)[c] Before | M.D.$\epsilon$ ($cal \cdot \Omega^{-1}$)[c] After | $\Delta\theta$ ($\Omega$)[d] | $\theta$[e] ($\Omega$) | $\Delta T$[f] ($10^{-2}$ °C) | Corr. to[g] 298.15K ($cal \cdot mol^{-1}$) | $-\Delta H_{298.15\,K}$ ($cal \cdot mol^{-1}$) R.P.[h] | $-\Delta H_{298.15\,K}$ ($cal \cdot mol^{-1}$) M.D.[h] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 36H | 0.50278 | 698 | – | 105.29 | – | 105.28 | 0.075 | 22.380 | 28.045 | 0.0 | 7114.2 | 7113.9 |
| | | 712 | – | 105.32 | – | 105.32 | 0.075 | | 28.045 | | 7116.3 | 7116.1 |
| [k]37H | 0.50480 | 662 | – | 105.24 | – | 105.30 | 0.013 | 22.327 | 28.056 | 0.0 | 7085.3 | 7087.4 |
| | | 672 | – | 105.26 | – | 105.32 | 0.018 | | 28.049 | | 7087.1 | 7089.3 |
| 38H | 0.49639 | 705 | – | 105.29 | – | 105.30 | 0.083 | 22.099 | 27.679 | 0.0 | 7111.6 | 7112.7 |
| | | 720 | – | 105.33 | – | 105.34 | 0.083 | | 27.679 | | 7114.4 | 7115.6 |

[a]Stirring Speeds: L = Low; M = Medium; and H = High.
[b]K is the heat leakage constant for experiment and calibration, respectively.
[c]R.P.$\epsilon$ and M.D.$\epsilon$ are the electrical energy equivalents using the Regnault-Pfaundler and modified Dickinson calculation methods, respectively. The top and bottom values are taken from the LKB and DVM electrical energy measurement stations, respectively.
[d]$\Delta\theta$ is the stirring energy correction. The top and bottom values are for the R.P. and M.D. calculation methods, respectively.
[e]$\theta$ is the uncorrected reaction resistance change.
[f]$\Delta T$ is the corrected reaction temperature change. The top and bottom values are for the R.P. and M.D. calculation methods, respectively.
[g]Correction to 298.15K using $C_p = 41.55\ cal \cdot deg^{-1} \cdot mol^{-1}$.
[h]The top and bottom $\Delta H$ values correspond to LKB and DVM $\epsilon$ respectively.
[i]Vented reaction vessel.
[j]Battery power supply
[k]$CO_2$ purged HCl.